

Reinforcement of Hydroxypropylcellulose Films by Cellulose Nanocrystals in the Presence of Surfactants

Noor Rehman^{a, b*}, Maria Inez G. de Miranda^{a, c}, Simone M. L. Rosa^a and Clara I. D. Bica^{a*}

^a Instituto de Química, Universidade Federal do Rio Grande do Sul, 91501-970, Porto Alegre/RS, Brazil

^b Department of Chemistry, Shaheed Benazir Bhutto University, 18000, Sheringal Dir (Upper) KPK, Pakistan

^c Instituto de Ciências Exatas e Tecnológicas, Universidade FEEVALE, Campus II, 93525-075, Novo Hamburgo/RS, Brazil

Abstract Hydroxypropylcellulose (HPC) films were prepared by casting with cellulose nanocrystals in the presence of anionic surfactant sodium dodecylsulphate (SDS) and cationic surfactant hexadecyltrimethyl ammonium bromide (CTAB). The cellulose nanocrystals were isolated from maize straw, a biomass source produced in huge quantities as an agrowaste in Brazil. These bionanocomposite films had good transparency and their surface hydrophilic character was evidenced by static contact angle measurements. Thermogravimetry (TGA) measurement revealed that nanocrystals and surfactants changed the thermal stability of the HPC films. Dynamic mechanical analysis (DMA) showed that the tensile storage and loss moduli of the HPC films increased by increasing the contents of cellulose nanocrystals and surfactants, especially in the case of CTAB. This good reinforcing effect of HPC matrix can be explained as due to electrostatic attractive interactions brought about by the presence of CTAB and the nanocrystals.

Keywords: Hydroxypropylcellulose; Cellulose nanocrystals; Bionanocomposites; Maize straw; Micellization.

INTRODUCTION

The application of cellulose nanocrystals as reinforcement in nanocomposites has attracted significant attention due to the need for developing sustainable biobased products and taking into account the emerging shortage of petroleum. Indeed the renewable nature, abundance and good mechanical properties of cellulose are well recognized^[1, 2]. These properties arise from the β -1,4 linked glucopyranose chains, aligned as crystalline domains by intra- and intermolecular hydrogen bonds and surrounded by amorphous domains. Cellulose nanocrystals are rigid rodlike nanoparticles usually prepared by acid hydrolysis so that the amorphous domains are removed, leaving behind only the crystalline ones^[3]. The large specific surface area of cellulose nanocrystals, also called whiskers (WH) or nanowhiskers, is largely appreciated being them frequently named as bionanofillers. Cellulose nanocrystals constitute one type of nanocellulose. Many properties, especially the size of the nanocrystals, depend on the source of the starting cellulose materials, the temperature and the duration of hydrolysis^[4–7]. When acid hydrolysis is conducted with sulfuric acid (64 wt%), the nanocrystal surface becomes negatively charged but when hydrochloric acid is used, charged groups are essentially not introduced^[8]. The homogeneous dispersion of the nanocrystals within the polymer matrix, the strong interactions and adhesion between them have resulted in improving the mechanical properties of bionanocomposites or nanocomposites^[9–11]. This homogeneous dispersion is indeed required to obtain well-defined mechanical properties and consistent performance of the final nanocomposite material. Aggregation of the dispersed phase has a negative impact

* Corresponding authors: Noor Rehman, E-mail: noor_rehman33@yahoo.com

Clara I. D. Bica, E-mail: claraism@iq.ufrgs.br

Received April 18, 2016; Revised May 25, 2016; Accepted June 6, 2016

doi: 10.1007/s10118-016-1844-y

resulting in undesirable effects on the final composite, acting aggregates as stress concentrators^[11, 12]. It is known that cellulose nanocrystals have a natural tendency to aggregate^[4, 7, 10, 13]. In order to prevent this aggregation and to improve their dispersion in the polymer matrix, modification of the surface of cellulose nanocrystals is required. For this purpose, some procedures include grafting^[14], silylation of —OH groups^[15] and the use of surfactants^[13, 16, 17] are adopted. In the last few years other fields for the application of cellulose nanocrystals have been suggested as for example water purification, drug delivery, human tissue and bones' regeneration as well as catalysis^[8, 12, 18, 19].

Hydroxypropylcellulose (HPC) is cellulose ether that does not show any cytotoxicity and was approved by the Food and Drug Administration (FDA) to be used in drug delivery^[20]. Hydrogels of HPC are temperature responsive: they shrink if the temperature rises above its lower critical solution temperature (LCST) and expand, by swelling in water, if the temperature is below LCST^[20, 21]. Reported values of LCST of HPC are near the physiological temperature: they vary between 37 and 42 °C^[20, 22]. Due to these fascinating properties, HPC was chosen as the polymer matrix in this work. In the literature there are only a few articles about the effect of nanocellulose on HPC films, as for example nanofibrillated and fibrillated TEMPO-oxidized celluloses^[23, 24]. However, to our knowledge, the effect of surfactant modified cellulose nanocrystals on HPC films was not yet reported.

The aim of this work is to study the effect of surfactant modified cellulose nanocrystals inside hydroxypropylcellulose (HPC) matrix, understanding the interactions among the different components and the reinforcing potential on the HPC bionanocomposite films by using thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The nanocrystals isolated from maize straw cellulose as described previously^[4] were negatively charged due to the presence of sulfate groups on the surface. It was shown^[4] that these nanocrystals have a length of $L = (388 \pm 43)$ nm, a thickness of $d = (19 \pm 2)$ nm resulting an aspect ratio of 20, as is the case of some other vegetable sources^[12]. The anionic sodium dodecylsulfate (SDS) and the cationic hexadecyltrimethylammonium bromide (CTAB) surfactants were chosen for this study due to their widespread use in science and technology.

EXPERIMENTAL

Materials

Hydroxypropylcellulose (HPC) with nominal weight-average molecular weight (M_w) of 1×10^5 g·mol⁻¹ was purchased from Sigma-Aldrich ((Milwaukee, WI, USA). Cellulose nanocrystals were prepared from maize straw^[4] which was supplied by the agronomic experimental station of Federal University of Rio Grande do Sul (UFRGS). Sodium dodecylsulphate (SDS, 98% of purity) was purchased from Acros Organics and cationic surfactant hexadecyltrimethylammonium bromide (CTAB, $\geq 98\%$ of purity) was purchased from Sigma Aldrich, both were used without further purification.

Preparation of Cellulose Nanocrystals

Purified cellulose from maize straw was treated with a 64 wt% H₂SO₄ solution. The acid hydrolysis was carried out for 150 min, at room temperature, under constant stirring. The reaction was terminated by adding cold deionized water. After 1 h of centrifugation, the suspension was ultrasonicated in order to get uniform dispersion. The excess of sulfuric acid was removed by dialysis of the nanocrystal suspension against deionized water until neutral pH. The detailed procedure was described previously^[4].

Preparation of Nanocrystal-surfactant Aqueous Systems

At first, an aqueous suspension with 0.3 g·L⁻¹ of maize straw cellulose nanocrystals was prepared at room temperature. Aqueous solutions of surfactants (SDS or CTAB) were produced in this nanocrystals' suspension in a way to keep the concentration of surfactant in the range from 0.5 mmol·L⁻¹ to 10 mmol·L⁻¹. This range of concentrations was chosen because the critical micelle concentration (CMC) of each surfactant lies in this range. Each system was kept at 24 h under stirring, so that clear nanocrystal-surfactant suspensions were obtained.

Preparation of Bionanocomposite Films

Bionanocomposites were obtained by the casting method given below. The HPC solution (3 wt%) was prepared by dissolving 1.5 g of HPC in 50 mL of deionized water. The solution was stirred overnight to ensure complete dissolution of the polymer. Films with 5 wt% and 10 wt% of nanocrystals were prepared at room temperature by mixing appropriate volumes of 3.0 wt% aqueous solution of HPC with 0.3 g·L⁻¹ aqueous suspension of maize straw nanocrystals. The 5.0 wt% nanocrystal content was chosen for further preparations using two different surfactants (SDS or CTAB) and it was followed the procedure described in the previous section. The final systems were maintained under constant stirring during four hours at room temperature. The suspensions were transferred into Petri dishes and placed in an exsiccator where they were slowly degassed under vacuum. These bionanocomposite films were left to dry for several days until constant weight. The films were then cut to appropriate sizes for thermogravimetric (TGA) and dynamical mechanical (DMA) analyses. Before the analyses, the films were stored under dry atmosphere in an exsiccator.

Characterization of Films

Static water contact angle (WCA) was measured at room temperature using 4–6 µL droplet of deionized water by gently depositing it on the surface of films using a microsyringe. All the measurements were repeated at least twice and at different positions. The images were captured using a Digital Blue microscope (QX5) having a digital video camera and analyzed for static contact angle measurements using Surftens 3.0 software. The WCA values reported were averages of six measurements performed in different areas of each sample surface. Special care was taken so as to measure the static contact angle as quickly as possible due to the film solvency in water.

TGA measurements were conducted from 30 °C to 700 °C at a heating rate of 20 K·min⁻¹ under inert atmosphere of N₂ (flux: 50 mL·min⁻¹), using a TA Instruments model TGA Q5000 IR. Sample weight was around 7 mg. The TGA microbalance had a precision of (± 0.1) µg.

DMA analysis was made using an analyzer DMA Q800 V7.0 Module Multi-Frequency, TA Instruments. The measurements were performed with a frequency of 1 Hz using a strain rate of 0.1% in tensile mode. The temperature was scanned at 3 K·min⁻¹ from -30 °C to 150 °C. The average thickness of the specimens was around 0.45 mm, the width was 7.2 mm and the length was 10–12 mm. The storage (*E'*) and loss (*E''*) moduli were determined.

RESULTS AND DISCUSSION

Visual Aspect and Hydrophilicity of Films

As can be seen in Fig. 1 the neat HPC films have good transparency. After adding cellulose nanocrystals, alone or with surfactant, this visual transparency of HPC films slightly decreased.

The surface hydrophilicity of films (HPC and bionanocomposites) was evaluated by static contact angle (θ) measurements (as also presented in Fig. 1 at the first set of images). It is well known that an increasing in wettability/hydrophilicity of films can be associated with decrease in static contact angles ($\theta \leq 90^\circ$) between the film surface and the liquid drop. In Table 1 it can be observed that the contact angle of HPC neat film is 64.7°, a value that agrees well with that reported in the literature^[25]; in the presence of nanocrystals the contact angle decreases to the value of 59.8°. Analyzing this behavior, the addition of WH into HPC matrix results in an increase of surface hydrophilicity. After adding surfactants there is a marked decrease in the contact angle which is more pronounced in the case of CTAB being the lowest value of 23.5°. It can be concluded that the surface became more hydrophilic.

It has been reported that, due to the hydrophilic character of cellulose ethers, starches and chitosan, their films are water sensitive and show low moisture barrier properties which are adequate, for example, for the packaging of edible fresh vegetables or ornamental crops. Also due to this hydrophilicity, the films provide efficient barriers against hydrocarbons, oils and lipids^[9, 26–28]. Biopolymers are also important in agriculture where they are used as mulching films and fruit protection bags^[29] while in printing industry biopolymer coatings improve the paper and paperboard printability^[30]. Taking into account that the bionanocomposite films

developed in the present study show enhanced hydrophylic character, they may be suitable for applications in agriculture, packaging, food and printing industries.

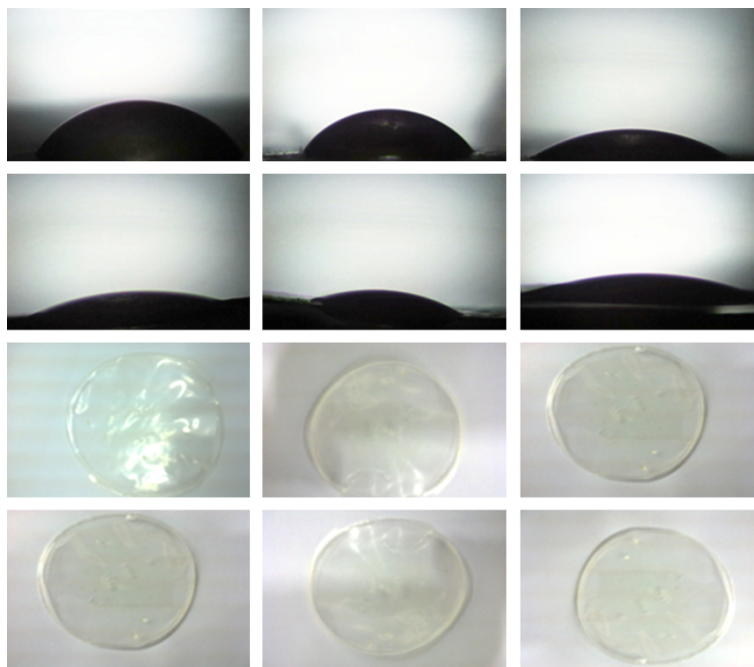


Fig. 1 Photographs of HPC films (bottom) and static contact angle of water at 20 °C on HPC films at the top (from left in first line) neat HPC, HPC+WH*, HPC+WH+1 mmol·L⁻¹ SDS and from left in the second line are HPC+WH+5 mmol·L⁻¹ SDS, HPC+WH+1 mmol·L⁻¹ CTAB and HPC+WH+5 mmol·L⁻¹ CTAB (The WH stands for whiskers, *i.e.* cellulose nanocrystals, and its concentration was 5 wt%.)

Table 1. Static contact angle of water at 20 °C on HPC films and work of adhesion (mJ·m⁻²) determinations where WH stands for whiskers, *i.e.* cellulose nanocrystals

HPC film	Static contact angle (°) and mean deviation (°)	Work of adhesion (mJ·m ⁻²)
Neat HPC	64.7 ± 0.7	102.2
HPC+WH*	59.8 ± 0.5	108.2
HPC+WH*+5 mmol·L ⁻¹ SDS**	36.9 ± 0.7	129.6
HPC+WH*+10 mmol·L ⁻¹ SDS**	27.8 ± 0.5	135.7
HPC+WH*+1 mmol·L ⁻¹ CTAB**	28.5 ± 0.5	135.2
HPC+WH*+5 mmol·L ⁻¹ CTAB**	23.5 ± 0.3	138.0

* WH (5 wt% of nanocrystal); ** Surfactant presence

Considering the contact angle values, it is interesting to assess the adhesion characteristics between the bionanocomposite films and water by simply calculating the work of adhesion (w_a). It is defined as the work required to separate the liquid and solid phases, or the negative free energy associated with the adhesion of the solid and liquid phases. It can be determined through the Young-Dupre equation, as given by:

$$w_a = \gamma_L(1 + \cos\theta)$$

where θ is the contact angle and γ_L is liquid surface tension (for water, γ_L is 72.80 mJ·m⁻², at 20 °C).

The w_a values are shown in Table 1, where HPC neat value ($w_a = 102.2$ mJ·m⁻²) is consistent with reported values^[25]. The addition of nanocrystals (WH) into HPC matrix leads to a smooth increase of adhesion ($w_a = 108.2$ mJ·m⁻²). However, after adding surfactants the increase in adhesion becomes more pronounced, and in the

presence of CTAB and nanocrystals the HPC bionanocomposite shows the highest value of $138.0 \text{ mJ}\cdot\text{m}^{-2}$ for the work of adhesion. As observed in poly(vinyl alcohol) (PVA) nanocellulose composites^[12], an increase in adhesion is required in the area of bioadhesives indicating that these HPC bionanocomposites may be a promising material for human tissue replacement applications.

Thermogravimetric Analysis (TGA)

As TGA reveals the decomposition processes of a material when it is heated, and as the derivative curves of TGA (DTG) represent each step of a decomposition process as a peak, the thermal investigation was carried out. TGA and DTG curves obtained for the bionanocomposite films are presented in Fig. 2. It can be seen that a typical weight loss step in the temperature range from 30 °C to 150 °C occurred which can be attributed to the dehydration of physically adsorbed water. This mass loss was around 4.3 wt% and it was observed for all samples. The decomposition of HPC film takes place in the temperature range of 250–450 °C with weight loss of 86.1% and has shown a maximum temperature peak of 450 °C in the DTG curve.

The decomposition process of pure cellulose nanocrystals takes place in two steps, as also shown in the DTG curve (as an inset in Fig. 2). The first decomposition step of nanocrystals occurs in the range of 150 °C to 450 °C which can be related to the degradation of more accessible regions highly sulfated, where the weight loss was 58%. The second decomposition process was observed from 450 °C to 700 °C which corresponds to melting and decomposition of the crystalline region with a residual weight loss of 32%. The degradation pattern of nanocrystals in two steps has also been reported previously^[31].

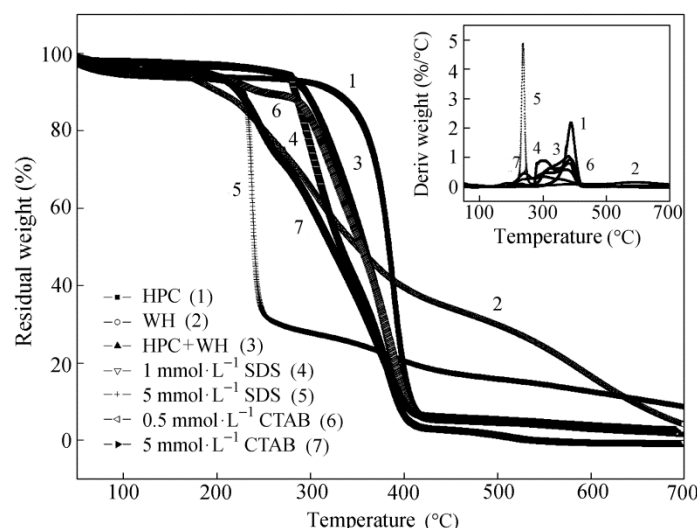


Fig. 2 TGA and DTG insert curves of neat HPC, HPC+WH*, HPC+WH+SDS (SDS = 1 and 5 $\text{mmol}\cdot\text{L}^{-1}$) and HPC+WH+CTAB (CTAB = 0.5 and 5 $\text{mmol}\cdot\text{L}^{-1}$) films (*WH (5 wt% of nanocrystal))

Moreover from the DTG curves it can be observed that important differences occur in films prepared without and with SDS surfactant. The latter presented multiple decomposition processes. The films of neat HPC, HPC+WH and HPC+WH+ 1 $\text{mmol}\cdot\text{L}^{-1}$ SDS showed a decomposition range at higher temperatures (300 °C to 480 °C) with a 91.2 wt% loss and a residual mass of 4.5 wt%. By using 5 $\text{mmol}\cdot\text{L}^{-1}$ of SDS, two narrow decomposition peaks were observed. The peak at lower temperature range (around 240 °C) could be related with the thermal decomposition of pure SDS: as reported by Ramimoghadam *et al.*^[32], it occurs from 160 °C to 380 °C. However the mass loss for this film is extremely high indicating that the polymer HPC itself is undergoing decomposition.

Analyzing the effect of CTAB on the HPC-based films (also in Fig. 2), TGA and DTG curves presented a typical weight loss step in the temperature range from 30 °C to 100 °C indicating the dehydration of adsorbed

water. These TGA curves show the multiple degradation process where the degradation patterns are very clear in the inset DTG curves (in Fig. 2). It is important to consider in HPC-CTAB films (0.5 and $5 \text{ mmol}\cdot\text{L}^{-1}$) that the thermal degradation of pure CTAB surfactant was observed from 180°C to 340°C , as reported in the literature^[32]. The HPC-CTAB film peaks detected at this range can be attributed to the CTAB presence and its particular decomposition.

Considering the DTG curves for both surfactants, it is possible to determine the T_{max} value corresponding to the temperature at a maximum rate of mass loss associated with each peak or decomposition step. For the HPC-based films, Table 2 presents the related T_{max} values that were obtained from DTG curves in the decomposition temperature range from 250°C to 450°C . The value of T_{max} of HPC main decomposition process decreased from 391°C to around 240°C with increasing concentration of CTAB or SDS surfactants. Due to a plasticizing effect, it was reported that a higher amount of surfactant solubilized in the polymer matrix leads to lower thermal stability and properties^[33]. In this work, considering the nanocrystals and surfactants' concentrations, the decomposition process of HPC bionanocomposite films, under heating, has shown that the thermal stability also decreased. However it can be attributed to a lubricant effect.

Table 2. HPC-based films and T_{max} values of main decomposition step as obtained from DTG curves

HPC Films	SDS T_{max} ($^\circ\text{C}$)	CTAB T_{max} ($^\circ\text{C}$)
HPC	391 ± 1	391 ± 1
HPC+WH	385 ± 2	385 ± 2
HPC+WH*+ $0.5 \text{ mmol}\cdot\text{L}^{-1}$ **	—	386 ± 1
HPC+WH*+ $1 \text{ mmol}\cdot\text{L}^{-1}$ **	378 ± 2	—
HPC+WH*+ $5 \text{ mmol}\cdot\text{L}^{-1}$ **	240 ± 1	375 ± 2

* WH (5 wt% of nanocrystal); ** Surfactant presence

Dynamic Mechanical Analysis (DMA)

The DMA study was made to verify how maize straw nanocrystals as well as surfactants influence dynamic mechanical properties of HPC films, namely tensile storage modulus E' (which indicates the elastic behavior of the HPC polymer matrix) and loss modulus E'' (which indicates the viscous behavior of the HPC polymer matrix). First of all, the effect of the nanocrystal concentration (at 5 wt% and 10 wt%) in HPC matrix was investigated over the glassy experimental temperature range (lower than 80°C) as assigned in Fig. 3. In this figure it can be seen that the addition of nanocrystals has significantly increased the storage modulus (E') of HPC matrix. In Fig. 3 an inset is presented where the E'' behavior can also be analyzed. It can be seen that in neat HPC curve there are two characteristic relaxations: α_{HPC} (from -20°C to 20°C), where the film exhibits a loss modulus peak attributed to the glass transition region of HPC, as well as γ_{HPC} (from 30°C to 80°C) a secondary relaxation that is characterized by exhibiting a remarkable softening of the films and that corresponds to the broad transition related to the formation of a liquid crystalline phase induced by the solvent during the film casting process^[34, 35]. The α_{HPC} and γ_{HPC} relaxations are presented in both HPC+WH films, but at 10 wt% nanocrystal concentration the γ_{HPC} relaxation was not so clearly observed as it was the case of the α_{HPC} relaxation. The rigidity of this cellulosic network is certainly due to interchain interactions in the form of hydrogen bonding which can be originated between nanocrystals (sulfate groups) and HPC matrix (hydroxyl groups).

In Fig. 4, in comparison to the HPC film where nanocrystals are present, it can be seen that adding SDS surfactant did not increase the tensile storage modulus. The nanocrystal concentration in SDS/HPC films was 5 wt%. However, at the SDS concentration of $5 \text{ mmol}\cdot\text{L}^{-1}$, the loss modulus (E'') increased as shown in the inset of Fig. 4. So, if the loss modulus E'' behavior of HPC+WH film is compared to those where SDS is present ($1 \text{ mmol}\cdot\text{L}^{-1}$ and $5 \text{ mmol}\cdot\text{L}^{-1}$), at the lowest concentration it can be concluded that SDS acts as a lubricant to the HPC+WH film, but at the highest concentration SDS enhances the reinforcement effect of the nanocrystals. This indicates a good dispersion of the nanocrystals in the HPC matrix. Recently Fu *et al.* have also obtained homogeneous dispersion of cellulose nanocrystals in chitosan matrix^[36], which resulted from hydrogen bonding

interactions between chitosan chains and CNCs. The nanocomposites CNC/chitosan were also prepared by casting and the static mechanical properties were improved by the reinforcement effect of the CNCs.

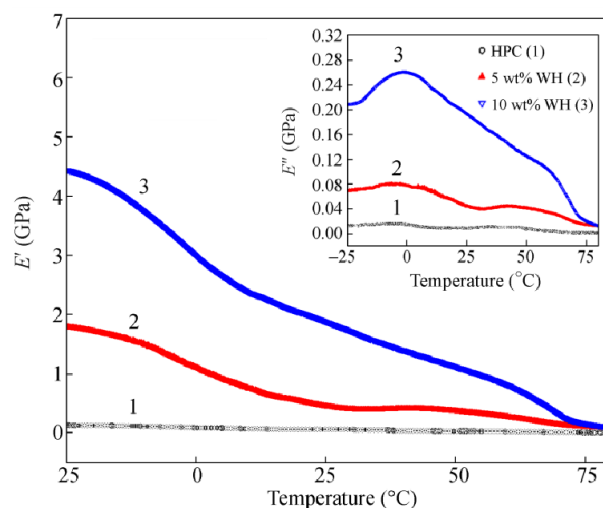


Fig. 3 Storage modulus (E') and loss modulus (E'') insert curves as a function of temperature, curves for neat HPC and HPC+WH (5 wt% and 10 wt%) films

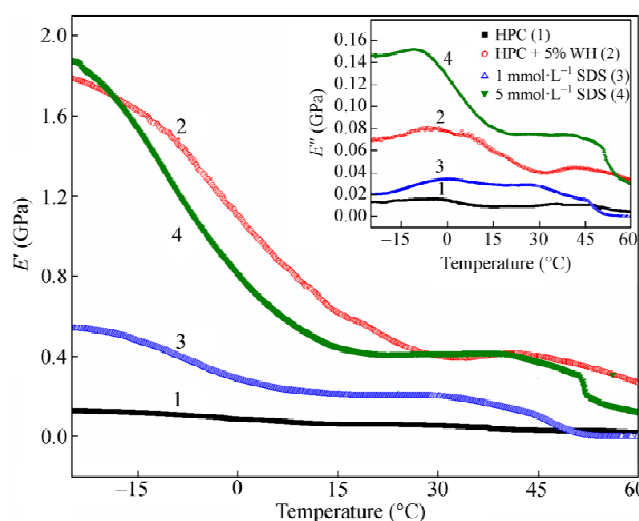


Fig. 4 Storage modulus (E') and loss modulus (E'') insert as a function of temperature, curves for neat HPC, HPC+WH*, HPC+WH +1 mmol·L⁻¹ SDS and HPC+WH +5 mmol·L⁻¹ SDS films. *WH (5 wt% of nanocrystal)

In Fig. 5 the influence of the cationic surfactant CTAB on the behavior of storage (E') and loss (E'') moduli of the HPC film is shown. The nanocrystal concentration in CTAB/HPC films was 5 wt%. From this figure, it can be seen that the simultaneous addition of nanocrystals and CTAB surfactant significantly affected the storage modulus of the HPC film. However, the capability of nanocrystals' reinforcement is evident only at the highest concentration of CTAB (5 mmol·L⁻¹), as far as there is an increase of the storage modulus of HPC bionanocomposite film. According to the literature, CTAB has critical micelle concentration (CMC) of around 0.92 mmol·L⁻¹ in aqueous solution at 25 $^{\circ}\text{C}$ ^[37, 38]. So it can be concluded that at the lowest concentration of CTAB (0.5 mmol·L⁻¹) micelles are not yet formed.

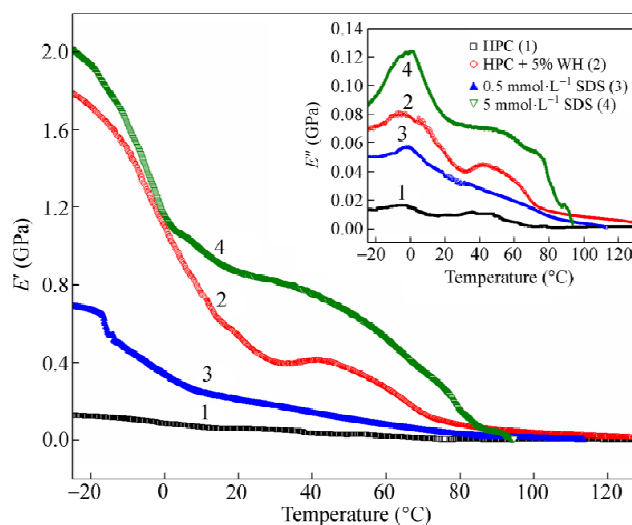


Fig. 5 Storage modulus (E') and loss modulus (E'') insert as a function of temperature, curves for neat HPC, HPC+WH*, HPC+WH+0.5 mmol·L⁻¹ CTAB and HPC+WH+5 mmol·L⁻¹ CTAB films
*WH (5 wt% of nanocrystal)

If the loss modulus E'' behavior of the HPC+WH film is compared to films where the cationic surfactant was added, a lubricant effect can be seen at the concentration 0.5 mmol·L⁻¹ while reinforcement arises at 5 mmol·L⁻¹. The latter can be interpreted as due to the formation of micelles and aggregates of nanocrystals/CTAB/HPC. Reinforcement is not observed in the film at CTAB = 0.5 mmol·L⁻¹ maybe because micelles were not previously formed in solution.

The two dynamic mechanical relaxations (α_{HPC} and γ_{HPC}) of neat HPC film were maintained in HPC/nanocrystal/CTAB and HPC/nanocrystal/SDS films where the γ_{HPC} relaxation seems to be differently affected by the surfactant. Besides the different aggregation conditions expressed by the use of cationic surfactant concentrations below or above its CMC, it must be highlighted that in the HPC/nanocrystal/CTAB system there are electrostatic attractions between the negatively charged sulfate groups of the nanocrystal surface and the positively charged head group of CTAB. In the case of HPC/nanocrystal/SDS films, the reinforcement capability is not as pronounced as that observed in HPC/nanocrystal/CTAB ones, probably due to electrostatic repulsive interactions between the sulfate groups both of the nanocrystals and the SDS head group.

CONCLUSIONS

Bionanocomposites of hydroxypropylcellulose (HPC), prepared with maize straw cellulose nanocrystals and surfactant SDS or CTAB, were well characterized in thermal and dynamic mechanical properties and related to their visual and surface aspects. The visual aspect of the bionanocomposite films evidenced the homogeneous dispersion of the nanocrystals in the HPC matrix at lower surfactant concentrations. The surface aspect was studied by static contact angle measurements, where an increase in surfactant content on films—independently of type of surfactant (SDS or CTAB)—led to a remarkable surface hydrophilicity to the bionanocomposites and an increasing of work of adhesion between water and film surface.

The TGA analysis revealed that the addition of nanocrystals and surfactants influenced the thermal stability of the bionanocomposite films. Irrespective of the type of surfactant, the decomposition of bionanocomposite HPC films began at lower temperatures (about 150 °C) than the neat HPC film (about 250 °C). This fact should not hinder new applications for the bionanocomposites because significant reinforcement behavior was observed in a temperature range lower than 80 °C by DMA. It was seen that the addition of nanocrystals and surfactants into the HPC polymer matrix increased the tensile storage (E') and loss moduli (E''). So a good dispersion of

maize straw cellulose nanocrystals in the HPC polymer matrix occurred and the compatibility between nanocrystals and HPC was improved when SDS and CTAB surfactants were used.

Besides, bionanocomposite films with CTAB possessed higher E' values when compared to films where SDS is present. This behavior can be explained as due to the electrostatic attractive interactions in the bionanocomposites with CTAB.

ACKNOWLEDGMENTS The authors would like to thank TWAS/CNPq, CNPq, CAPES, CAPES/REUNI, for fellowships, Prof. Dr. Daniel E. Weibel (IQ/UFRGS) for allowing the use of the static contact angle equipment (IQ/UFRGS) and Prof. Dr. Marcos A. Villetti (UFMS) for helpful discussion. Dr. S.M.L. Rosa thanks Prof. Dr. Nadya P. da Silveira for the accordance to collaborate in the present project.

REFERENCES

- 1 Brinchi, L., Cotana, F., Fortunati, E. and Kenny, J., *Carbohydr. Polym.*, 2013, 94: 154
- 2 Moon, R.J., Martini, A., Nairn, J., Simonssen, J. and Youngblood, J., *Chem. Soc. Rev.*, 2011, 40: 3941
- 3 Siqueira, G., Bras, J. and Dufresne, A., *Biomacromolecules*, 2009, 10: 425
- 4 Rehman, N., Miranda, M.I.G., Rosa, S.M.L., Pimentel, D.M., Nachtigall, S.M.B. and Bica, C.I.D., *J. Polym. Environ.*, 2014, 22: 252
- 5 Rosa, S.M.L., Rehman, N., Miranda, M.I.G., Nachtigall, S.M.B. and Bica, C.I.D., *Carbohydr. Polym.*, 2012, 87: 1131
- 6 Elazzouzi-Hafraoui, S., Nishiyama, Y., Putaux, J.L., Heux, L., Dubreuil, F. and Rochas, C., *Biomacromolecules*, 2008, 9: 57
- 7 Dong, X., Revol, J.F. and Gray, D., *Langmuir*, 1998, 5: 19
- 8 Araki, J., *Soft Matter*, 2013, 9: 4125
- 9 Bilbao-Sainz, C., Bras, J., Williams, T., Senechal, T. and Orts, W., *Carbohydr. Polym.*, 2011, 86: 1549
- 10 Jiang, L., Morelius, E., Zhang, J., Wolcott, M. and Holbery, J., *J. Compos. Mat.*, 2008, 42: 2629
- 11 Ljungberg, N., Bonini, C., Bortolussi, F., Boisson, C., Heux, L. and Cavaillé, J.Y., *Biomacromolecules*, 2005, 6: 2732
- 12 Kalia, S., Dufresne, A., Cherian, B.M., Kaith, L., Averous, L., Njuguna, J. and Nassiopoulos, E., *Int. J. Polym. Sci.*, 2011, 2011: 1
- 13 Heux, L., Chauve, G. and Bonini, C., *Langmuir*, 2000, 16: 8210
- 14 Peng, B., Han, X., Liu, H., Berry, R.C. and Tam, K.C., *Colloids Surf. A*, 2013, 421: 142
- 15 Gousse, C., Chanzy, H., Excoffier, G., Soubeyrand, L. and Fleury, E., *Polymer*, 2002, 43: 2645
- 16 Bonini, C., Heux, L., Cavaillé, J. Y., Lindner, P., Dewhurst, C. and Terech, P., *Langmuir*, 2002, 18: 3311
- 17 Bondeson, D. and Oksman, K., *Compos. Interfaces*, 2007, 14: 617
- 18 Jackson, J.K., Letchford, K., Wasserman, B.Z., Ye, L., Hamad, W.Y. and Burt, H.M., *Int. J. Nanomed.*, 2011, 6: 321
- 19 Cunha, I.T., Teixeira, I.F., Mesquita, J.P., Ardisson, J. D., Binatti, I., Pereira, F.V. and Lago, R.M., *J. Braz. Chem. Soc.*, 2016, 27: 363
- 20 Hoo, S.P., Sarvi, F., Li, W.H., Chan, P.P.Y. and Yue, Z., *ACS Appl. Mater. Interfaces*, 2013, 5: 5592
- 21 Tokarev, I. and Minko, S., *Soft Matter*, 2009, 5: 511
- 22 Martins, R.M., Silva, C.A., Becker, C.M., Samios, D., Christoff, M. and Bica, C.I.D., *J. Braz. Chem. Soc.*, 2006, 17: 944
- 23 Eyholzer, C., Lopez-Suevos, F., Tingaut, P., Zimmermann, T. and Oksman, K., *Cellulose*, 2010, 17: 793
- 24 Johnson, R.K., Zink-Sharp, A., Renneckar, S.C. and Glasser, W.G., *Cellulose*, 2009, 16: 227
- 25 Luner, P.E. and Oh, E., *Colloids Surf. A.: Physicochem. Eng. Aspects*, 2001, 181: 31
- 26 Fernández-Pan, I. and Caballero, J.I.M., "In biopolymers-new materials for sustainable films and coatings", 1st ed., Plackett, D., ed.; Wiley, Chichester, UK, 2011, p. 233
- 27 Lavoine, N., Desloges, I., Dufresne, A. and Bras, J., *Carbohydr. Polym.*, 2012, 90: 735
- 28 Comas, V., *Polímeros*, 2013, 23: 287

- 29 Martín-Closas, L. and Pelacho, A. L., "In biopolymers-new materials for sustainable films and coatings", 1st ed., Plackett, D., ed.; Wiley, Chichester, UK, 2011, p. 277
- 30 Aulin, C. and Lindstrom, T., "In biopolymers-new materials for sustainable films and coatings", 1st ed., Plackett, D., ed, Wiley, Chichester, UK, 2011, p. 255
- 31 Silverio, H.A., Flauzino Neto, W.P., Dantas, N.O. and Pasquini, D., *Ind. Crops Prod.*, 2013, 44: 427
- 32 Ramimoghdam, D., Hussein, M.Z.B. and Taufiq-Yap, Y.H., *Int. J. Molec. Sci.*, 2012, 13: 13275
- 33 Dalmas, F., Cavaille, J.Y., Gauthier, C., Chazeau, L. and Dendievel, R., *Compos. Sci. Technol.*, 2007, 67: 829
- 34 Miranda, M.I.G., Samios, D., Freitas, L.L. and Bica, C.I.D., *Polímeros*, 2013, 23: 1
- 35 Rials, T.G. and Glasser, W., *J. Appl. Polym. Sci.*, 1988, 36: 749
- 36 Geng, C.Z., Hu, X., Yang, G.H., Zhang, Q., Chen, F., and Fu, Q., *Chinese J. Polym. Sci.*, 2015, 33(1): 61
- 37 Holmberg, K., Jonsson, B., Kronberg, B. and Lindman, B., "Surfactants and polymers in aqueous solution", 2nd ed., Wiley, Chichester, UK, 2002, p. 221
- 38 Rehman, N., Khan, A., Bibi, I. and Siddiq, M., *Chinese J. Polym. Sci.*, 2012, 30(2): 217